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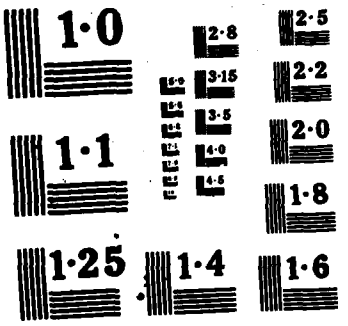

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Interim Technical Report

February 2, 1983 - May 31, 1984

Experimental Study of Electronic States at Metal-Dielectric Interfaces

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The method of attenuated total reflection has been used in the visible region to obtain precise values of the dielectric function of Ag films in contact with different dielectric media. By measuring, at eight visible laser wavelengths, the surface-plasmon resonance of an Ag film against air and then against an organic liquid, we show that for both cases the dielectric function can be described by the Drude model with the well-known frequency-dependent relaxation time. The observed change in the frequency dependent parameters appears to eliminate all previous models which have been proposed to describe this frequency dependent relaxation time. The observed changes are consistent with the idea of a complex relaxation time whose real and imaginary parts are connected in a casual way. The index-of-refraction dependence of the Drude parameters demonstrates that surface electrodynamics must play an important role.

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I. Abstract

Novel high resolution infrared techniques are used to explore the electronic states both at metal-dielectric interfaces and in ion implanted semiconductors.

II. Project Objectives

Development of the surface plasmon (SP) interferometer is one of our major objectives since it shows promise of being able to measure both the surface resistance and reactance of bare and coated metals in the infrared spectral region. The development of fine grating structures on metal surfaces for IR SP generation will continue. Particularly important is the dependence of the height of the SP above the grating with the grating amplitude. This quantity appears to play an important role in determining the efficiency of the SP interferometer. Since all previous infrared instruments have only measured the infrared surface resistance, this new surface technique will permit the first direct determination of the electron infrared mass, a quantity which appears in the theoretical dynamical models of metal surfaces and interfaces but which has remained experimentally elusive. Fabrication of the interferometer on single crystal metal surfaces will permit a spectroscopic study with high sensitivity of controlled oxide growth.

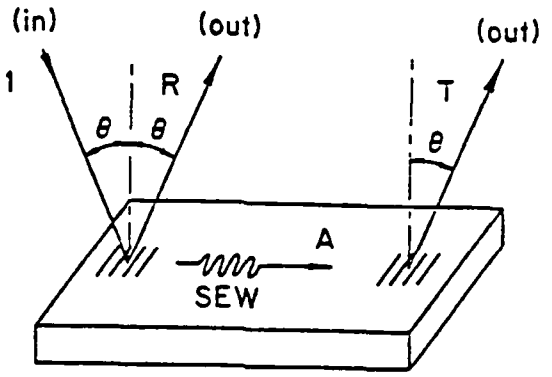
Another objective of our program is to carry out high resolution interferometric and laser spectroscopic measurements on thin films of defect states which are produced in bulk semiconductors by ion implantation. The purpose of such a study is twofold: 1) to measure the efficiency of spectral hole burning for possible application to frequency domain optical storage; and 2) to search in semiconductors for the analogue of the ultrasharp line spectra which have been produced by defects in dielectric crystals.

Accomplishments

A. Surface Electromagnetic Wave Spectroscopy on Metal Surfaces

At about the same time as the Russian group, Zhizhin et al,[1] showed that grating couplers together with broadband fourier transform spectroscopic techniques could be used to perform SEW spectroscopic measurements on bulk metal substrates, we began producing photolithographic gratings on metal substrates and testing the SEW coupling efficiency as a function of the groove depth of the grating. We found that grating couplers could be readily etched into single crystal W in about 3 sec with a mixture of 5 parts HF and 1 part HNO_3 and that these grating couplers were always more efficient than the dielectric edge coupler which had been used previously.[2] The elimination of the dielectric coupler is particularly important for SEW studies of single crystal samples of W in ultrahigh vacuum since the procedure for cleaning W is to heat it to about 2000°C with an electron beam. There is no dielectric IR coupler which can take such high temperatures.

A typical configuration for a SEW transmission measurement is shown in Figure 1. Bulk electromagnetic waves are incident on the grating at position I at angle θ, the reflected beam is labelled R. At a particular incident angle, frequency and grating spacing SEW's are generated on the metal surface. A second grating at the output intercepts the SEW's and converts them back into bulk electromagnetic waves. It is this relative intensity T which is measured by the detector. The lower part of the figure shows the signal measured at R and at T for a given frequency and as a function of angle, θ. Notice that the angle where the reflected beam shows a minimum is precisely the same angle where the SEW beam (T) shows a maximum. The throughput is about an order of magnitude larger than was obtained previously with the edge coupling technique.[2]



$1 = R + A + T$

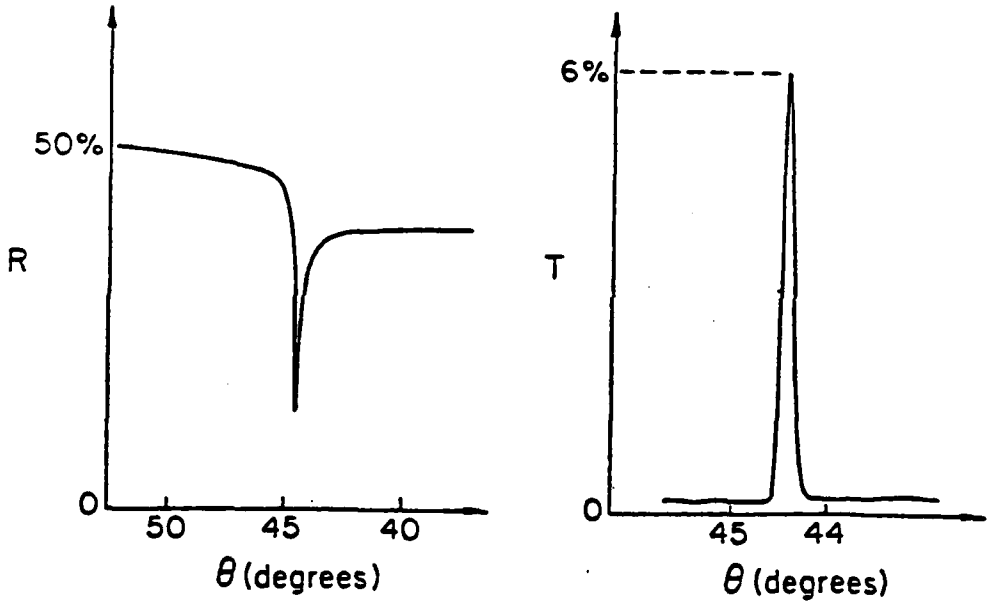


Figure 1. Surface electromagnetic wave (SEW) setup and data. The metal sample has two gratings etched in the surface. Plane waves incident on the grating (I) are either reflected (R) or transformed into SEW's which propagate along the metal surface to the output grating. The grating transforms the SEW's to plane waves (T) which are detected with a photoconducting element. The bottom of the figure shows typical data output for a single laser frequency as a function of angle . The angle at which the reflected beam (R) shows a sharp dip is exactly the same as the one where the transmitted beam shows a peak.

With the help of both AFOSR and NSF grants we have put together a general UHV system for a variety of SEW spectroscopic studies of clean, adsorbate and dielectric covered metals on which are etched grating couplers. A schematic diagram of the top view of the UHV system and associated IR optics is shown in Figure 2.

The stainless steel UHV chamber is 12" diameter x 4 1/2' high. The lower section contains a 220 ℓ/s ion pump and a titanium sublimation pump. Pressures of less than 10^{-10} Torr are routinely achieved in this system. The separable upper section contains a gas analyzer, a sputtering ion gun, LEED/Auger optics and a gas inlet valve. An x-y-z-θ manipulator is mounted on top to maneuver the 6 cm long W sample in the beam. The input and output gratings on the W sample shown are 5 cm apart.

Because we are making measurements with a strong laser source and it is the source noise not the detector noise which dominates, the signal to noise is optimized by maximizing the contrast. The spacing between the input and output gratings is made as large as possible in this limit.

The CO_2 laser can be replaced by a N_2O or CO laser or the frequencies can be doubled with a Teharmonic generator crystal.

As an example of the kind of data one can obtain with such a system we show the temperature dependence of the SEW signal for W over a very large temperature interval. The measured temperature dependence of the SEW signal at two different frequencies is shown in Figure 3. Note that for each frequency the data can be described by two exponentials.

At first this result appeared quite surprising to us because the theoretical SEW attenuation coefficient $\alpha(t)$ is simply related to the d.c. resistivity $\rho(T)$ by

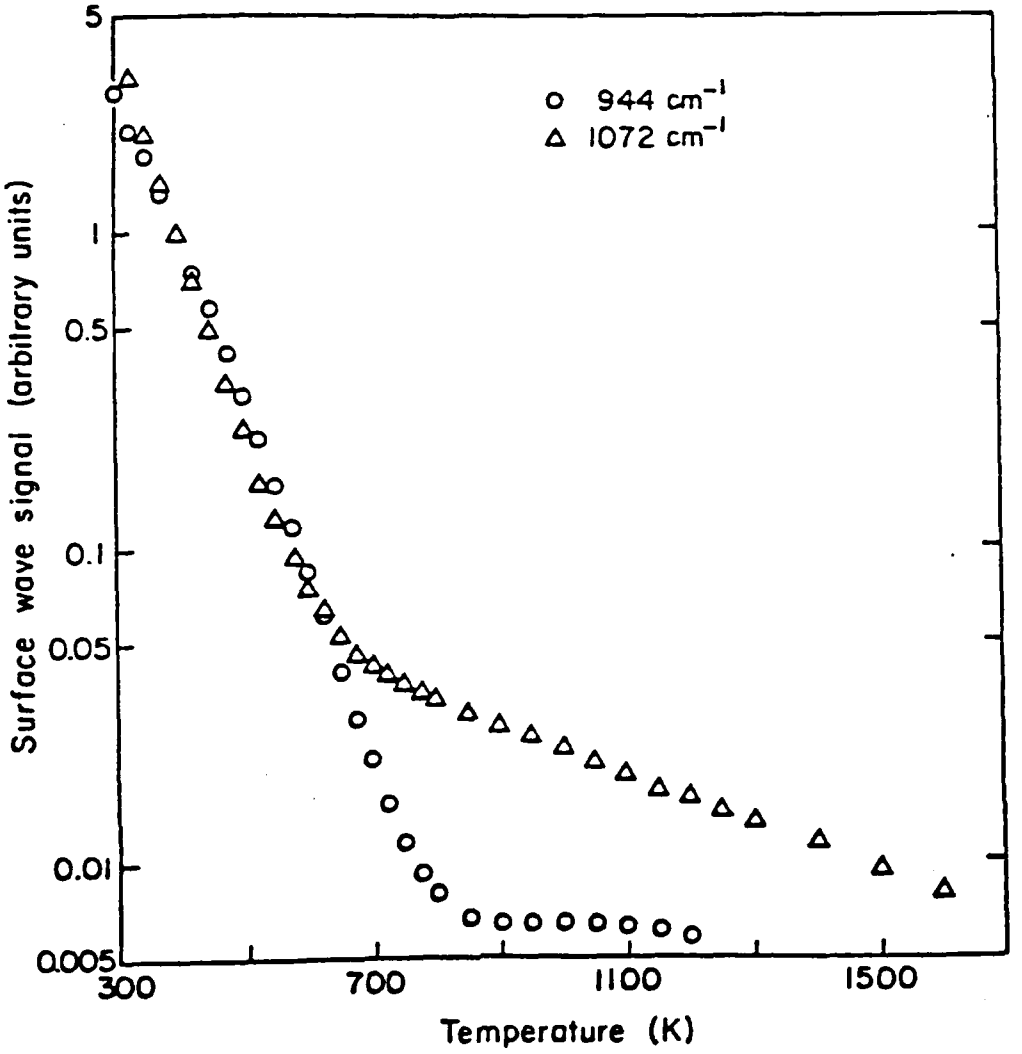


Figure 3. Surface wave signal on W vs. temperature for two different frequencies. Note that for each frequency the temperature dependence is described by two exponentials. The fast exponential at low temperature is due to the SEW attenuation and the slow exponential at high temperature is due to surface skimming plane waves.

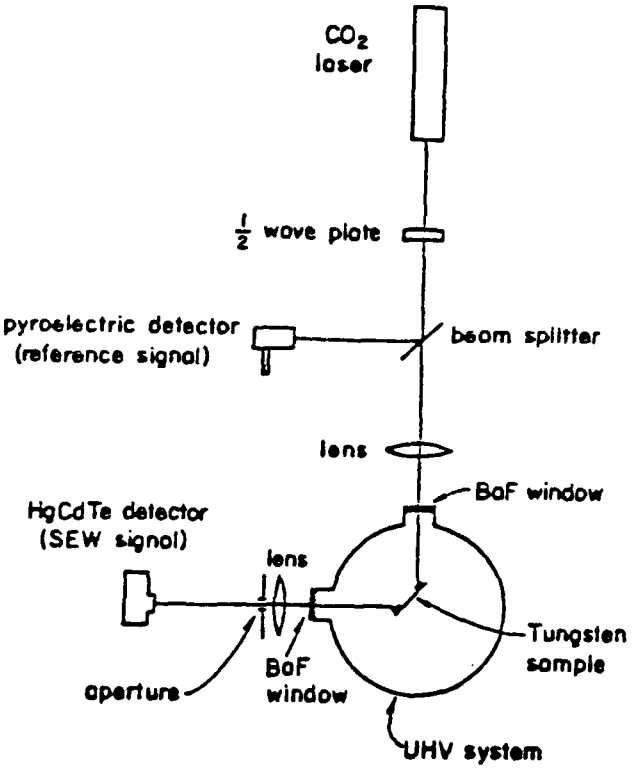


Figure 2. Schematic diagram of the UHV system with associated IR optics for the SEW measurement. The spacing between the two gratings on the single crystal tungsten sample is 5 cm. The various elements are labelled in the figure. (top view)

$$\alpha(T) = \frac{\omega^2}{4\pi c}\ \rho(T). \qquad (1)$$

where ω is the laser frequency, c the velocity of light and the d.c. resistivity varies linearly with T. Only one decay constant is to be expected in this case.

The large decay constant at low temperatures is mainly due to SEW waves while the small decay constant at large temperatures is mainly due to surface skimming electromagnetic waves in the vacuum. These waves are generated in the following way: The plane electromagnetic waves from the source interact with the grating and produce a surface electromagnetic wave on the grating which has a height, h_g, say. Because of the optical properties of the grating, itself, this height is smaller than the height of the SEW for a smooth metal surface, h_s. At the boundary between the smooth surface and the grating $\vec{E}$ and $\vec{H}$ tangential must be continuous at all distances above the metal surface. Because $h_g < h_s$ for the SEW mode on each side of the boundary plane waves must be generated in order to satisfy the boundary conditions. We were able to understand and interpret this effect very quickly because of our earlier work on the SEW interferometer[3] which was observed for metals coated with thin dielectric layers.

It now appears that an SEW interferometer can be constructed on a bare metal surface. A precise measurement of the null produced by the interference of the SEW beam and the plane wave beam uniquely determines the reactance of the metal in the infrared. All previous infrared measurements on metals have only measured the infrared resistance. Some exciting possibilities which made use of this new measuring technique are described in the proposal section.

B. The Optical Constants of Metal Mirrors

When calculating the reflectivity of a metal mirror coated with a dielectric it is always assumed that the optical constants of the metal do not influence the optical constants of the dielectric and vice versa. We have found this assumption (which had never been tested previously) to be incorrect. The problem was tackled in the following manner.

The method of attenuated total internal reflection was used in the visible to obtain precise values of the dielectric function of Ag films in contact with different dielectric media. By measuring, at eight visible laser wavelengths, the surface plasmon resonance of an Ag film against air and then against an organic liquid, we showed that for both cases the dielectric function can be described by the Drude model with the well known frequency dependent relaxation time,[4,5] namely, $\tau^{-1}(\omega) = \tau_0^{-1} + \beta\omega^2$. The interesting results are that $\tau_0^{-1}(\text{liquid}) > \tau_0^{-1}(\text{air})$, $\beta(\text{liquid}) < \beta(\text{air})$ and that the plasma frequency $\omega_p(\text{liquid}) > \omega_p(\text{air})$. All previous models [6-10] which have been proposed to describe this frequency dependent term appear to be eliminated by the fact that β changes, the sign of the change or its magnitude. The observed changes in β and ω_p are consistent with the idea of a complex relaxation time whose real and imaginary parts are connected in a causal way.[11] The index of refraction dependence of the Drude parameters demonstrates that surface electrodynamics must play an important role.

For the alkali metals it has been shown that a surface plasmon assisted photon absorption mechanism[12] which leads to an initial ω^4 dependence of the Drude scattering rate is consistent with the experimental data if the magnitude of the mechanism is used as a free parameter. It was also shown that increasing the index of refraction of the neighboring dielectric half space increases the strength of this term, increases λ and hence decreases ω_p.

The fact that the optical properties of the noble metals change in the opposite way when the index of refraction is increased is a clear indication that this mechanism cannot be the dominant factor here.

It has been known for some time that when a metal surface is probed with TM polarized radiation, electron-hole pair excitation should contribute to the optical absorption.[13-15] Recently, Ljungbert and Apell[16] have proposed that this effect can be described in terms of a single parameter, the first moment of the induced surface charge of the metal. From their calculation of the relative contribution of electron-hole pairs to the total absorptance, we can estimate the magnitude of the appropriate frequency dependent scattering rate which describes this process. It is not large enough to account for the measured results.

The large change in β required for the electron-hole excitation mechanism leads us to speculate on another possibility which again makes use of surface plasmons but now in an indirect role. The fact that the optical properties of the alkali metals and noble metals seem to change in opposite ways when the index of refraction of the half space changes may be simply an indication of the size of the electron-electron scattering term within the skin depth of each metal type. Inkson[17] has pointed out that although the surface plasmon interaction itself is attractive below the electrostatic mode limit, the decrease in the bulk plasmon exchange interaction near the surface causes the total interaction for quasi-particles to be more repulsive than in the bulk.

If, below the electrostatic mode frequency, electron-electron scattering dominates the surface plasmon mediated scattering within a skin depth for the noble metals while the converse is true for the alkali's then a consisent picture emerges. Increasing the index of the dielectric half space would

increase the strength of the attractive SP interaction for both metal types and decrease the magnitude of the electron-electron scattering term within a skin depth, but this decrease would only be apparent in the optical properties of the noble metals.

Since liquids absorb in the infrared spectral region a different kind of experimental test had to be used here. First the surface plasmon attenuation coefficient at 10 μm was measured for bare Ag and Au optically-thick films and found to be in good agreement with the Drude model predictions.[18] Next the surface-plasmon propagation characteristics of these same films are studied as a function of Ge overcoating thickness. The predicted linear dependence of the attenuation coefficients with Ge thickness is observed but the measured slopes, which are directly related to the plasma frequency of the metals, are almost a factor of 2 larger than theory can predict. Note that this apparent increase in the plasma frequency with increasing dielectric constant is of the same sign but much larger in magnitude than was found with the measurements in the visible region.

Another aspect of the thickness-dependence data which is important is that the straight line through the data extrapolates back to the bare metal SP value. If the mean free path of the electrons within a skin depth of the surface was reduced by the presence of the Ge in or on the metal, if scattering due to surface roughness was enhanced by the coating, or if interface states in the Ge were important, the straight line should extrapolate back to a value somewhat larger than the bare SP value. We conclude that the infrared measurements support the optical studies.

Although it has been known for many years that the Drude parameters of noble metal films depend on surface morphology and many relaxation processes have been invoked to explain the quadratic frequency dependence of the

electron relaxation frequency, it was not generally recognized that surface electrodynamics could play an important role in the visible and infrared spectral regions. Our systematic study of an index of refraction induced change in the Drude parameters of Ag films demonstrates that this is the case. More experiments need to be carried out to identify the physical process, but the general conclusion is now clear. The dielectric function required to describe the IR and optical properties of a free electron-like metal mirror depends on the dielectric constant of the adjoining medium.

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